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Wetting of doped carbon nanotubes by water droplets

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Abstract

We study the wetting of doped single- and multi-walled carbon nanotubes by water droplets using molecular dynamics simulations. Chemisorbed hydrogen is considered as a model of surface impurities. We study systems with varying densities of surface impurities and we observe increased wetting, as compared to the pristine nanotube case, attributed to the surface dipole moment that changes the orientation of the interfacial water.

We demonstrate that the nature of the impurity is important as here hydrogen induces the formation of an extended hydrogen bond network between the water molecules and the doping sites leading to enhanced wetting.
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1. Introduction

The potential development of devices based on carbon nanotubes (CNT) in nanofluidic chips, probes, and capsules for drug delivery [18,9] hinges on our understanding of their interaction with liquids and in particular with aqueous solutions. In addition the manufacturing of CNTs often involves surface impurities and it is important to include these in the modeling and characterization of the device.

Experiments by Dujardin et al. [6] indicates that liquids with a surface tension below 130–170 mN m^{-1} wet bundles of SWCNTs. This model [6], implying that pure water, with a surface tension of 72 mN m^{-1} at room temperature, should wet CNTs, is contrasted however, by the low solubility of CNT in water [2]. Recent experiments [12,11,10,16] involving aqueous solutions confined inside multi-walled carbon nanotubes (MWCNTs) dem-

onstrated a high degree of wetting. Specifically in [16] contact angles of 10–25° are reported. These MWCNTs, however, were produced by the hydrothermal method that often leads to ragged termination of the different graphene sheets with OH or COOH end-groups. These polar impurities are expected to affect the degree of wetting [10]. Also Rossi et al. [17] recently reported contact angles below 55° for water confined inside MWCNTs, and ascribed this low contact angle to hydrogen terminations of the graphene sheets in the large diameter MWCNTs produced by chemical vapor deposition.

Molecular Dynamics (MD) simulations [22] found a non-wetting behaviour for water droplets confined inside pristine SWCNTs. In a related study, Werder et al. [23] validated the interaction potentials to match the experimental contact angle of a water droplet on a pure graphite surface [8,5] quantifying its hydrophobic behaviour.

In this Letter, we employ MD simulations to study the influence of surface impurities, modeled as chemisorbed hydrogen, on the contact angle of water droplets confined inside single- and multi-walled carbon

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nanotubes. The presence of the hydrogen atoms at the doping site have two complementary characteristics: they induce a dipole moment that affects the polar water molecules, and present a docking site for the water to form additional hydrogen bonds. Here, we study both characteristics and quantify the influence of the dipole moment and the hydrogen bonding of the surface on the value of the contact angle. The results indicate consistent increased wetting for increased doping density. These results help in bridging the observation for hydrophobic behaviour observed in simulations of water and pristine CNTs and the experimental observations of hydrophilic behaviour of aqueous solutions confined inside doped CNTs.

2. Methodology

The water is modeled using the rigid SPC/E water model by Berendsen et al. [3], with an O–H bond length of 1 Å and a H–O–H angle of 109.47° constrained using the SHAKE algorithm [19]. The SPC/E model involves a Lennard-Jones potential between the oxygen atoms

$$U_{\alpha,\beta}(r_{ij}) = 4\epsilon_{\alpha,\beta}\left[\left(\frac{\sigma_{\alpha\beta}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r_{ij}}\right)^6\right], \quad \text{for } r_{ij} < r_c, \tag{1}$$

where r_c is the radius of truncation (chosen to be 1 nm, and $U_{\alpha\beta}(r_{ij}) = 0$ for $r_{ij} > r_c$), and α and β refers to the atomic species (here oxygen–oxygen: $\epsilon_{OO} = 0.6501$ kJ mol^{-1} and $\sigma_{OO} = 0.3166$ nm). The model includes a Coulomb potential acting between all atom pairs from different water molecules

$$U(r_{ij}) = \frac{q_i q_j}{4\pi\epsilon_0}\frac{1}{r_{ij}}, \tag{2}$$

where ϵ_0 is the permittivity in vacuum, and q_i is the partial free charge, $q_O = -0.8476$e and $q_H = 0.4238$e, respectively. These partial free charges describe the fixed, static dipole moment of water [3].

For the water–carbon interaction we use a Lennard-Jones potential between the carbon and oxygen atoms of the water, with values from Werder et al. [23] of $\epsilon_{CO} = 0.392$ kJ mol^{-1} and $\sigma_{CO} = 0.3190$ nm. These values reproduce the experimental macroscopic contact angle of water droplets in contact with a pristine graphite surface of 86° [23,8].

The doping of the CNTs by chemisorbed hydrogen is modeled by attaching a hydrogen atom to selected carbon atoms. The bond length between the hydrogen site (H_d) and the anchoring carbon atom (C_d) is set to 1.12 Å based on DFT calculations [14]. The doping site is described by a partial charge derived from quantum chemical calculations at the level of MP2 [21]. In order to account for the different models studied in [21] we will

here consider a range of charges, $q_{H_d} \in \{0.108, 0.162, 0.216\}$. The corresponding negative charge on the anchoring carbon atom is $q_{C_d} = -q_{H_d}$ to preserve electrical neutrality. The long range electrostatic interactions are treated using the Smooth Particle Mesh Ewald (SPME) technique [7]. A mesh resolution of 32^3 is found to be sufficient to accurately resolve the reciprocal part of the energy and corresponds to a mesh spacing of 0.33 nm in the computational box of $10.105 \times 10.105 \times 10.635$ nm.

We study the influence on the contact angle of the amount of doping (coverage) and on the modeling of the doped site by varying the partial charge. The results are presented in terms of radial profiles of the fluid density, the number of hydrogen bonds that water forms and the orientation of the water dipole moment. All the simulations (see Table 1) employ a timestep of 2 fs [20] and are conducted for 2 ns. The carbon nanotube is considered to be rigid to facilitate the sampling. This approximation is known to have little influence on the estimated contact angle [22]. During the first 0.2 ns the system is coupled to a Berendsen thermostat to achieve the desired temperature of 300 K. Statistics are collected from 0.3 to 2.0 ns in intervals of 0.2 ps with a total of 8500 samples. The standard deviation of the measured contact angle [22] is in all the cases less than 1.0°. The radial profiles are sampled in the bulk, central part of the droplet, with a height of 1 nm and a radial resolution of 100 bins. The criterium for the formation of hydrogen bonds has been adapted from [15] where we consider as an acceptor, the water oxygen atoms, and as a donor both other water molecules and the doping sites. The orientation of the dipole moment is characterized by the angle ϕ between the normal of the surface (pointing outwards) and the dipole moment of the water molecule. We compute the probability distribution as a function of $\cos(\phi)$ as described in [20].

Table 1
Simulations considered in the present study. $C(n,m)$ denotes the chirality of the CNT, L_d the bond length between the doping sites H_d and C_d in nm, δ the percentage of the doped carbon atoms and θ the contact angle

Case	$C(n,m)$	L_d (nm)	q_{H_d}(e)	δ (%)	θ (°)
1	(64,0)	–	–	0	96
2	(64,0),(72,0)	–	–	0	90
3	(64,0)	0.112	0.108	5	92
4	(64,0)	0.112	0.108	10	90
5	(64,0)	0.112	0.108	15	86
6	(64,0)	0.112	0.162	5	85
7	(64,0)	0.112	0.162	10	79
8	(64,0)	0.112	0.162	15	78
9	(64,0)	0.112	0.216	5	73
10	(64,0)	0.112	0.216	10	66
11	(64,0)	0.112	0.216	15	62
12	(64,0)	0.00112	21.6	15	74

3. Results and discussion

We study the wetting properties of water droplets confined inside doped SWCNT and MWCNTs. The SWCNT consists of a (64,0) CNT with radius 2.505 nm and the MWCNTs of two (64,0) and (72,0) CNTs, the latter with a radius of 2.818 nm. The water molecules are initially placed on a regular lattice with a density of 1 g cm^{-3} at 300 K, and occupy approximately 50% of the total volume of the CNT. The axial extent of the equilibrated droplet (5.38 nm) is sufficiently large to minimize the interaction between the two liquid–vapour interfaces. The surface impurities are randomly attached to the carbon surface with the constraint that any two doped carbon atoms are at least three bonds away. Hence, clustering of the doped sites in non-physical configurations [4], violating restrictions due to the double bonds in the carbon rings is avoided. As a consequence, the maximum possible coverage of the CNT is 18%.

In the reference simulation of the pristine system (case 1, see Table 1) the measured contact angle θ is 96° and compares well with the microscopic contact angle of 95° found in [23] for a water droplet on a pure graphite surface, indicating a negligible influence due to curvature. In addition we consider the influence of multiple carbon layers, by simulating a water droplet confined inside double-wall CNTs (case 2). For the pristine system we measure a contact angle of 90°. The smaller value as compared to the SWCNT (case 1) is attributed to the additional attraction that the water molecules experience from the outer CNT and is consistent with experimental observations [6] concerning the difference in the wetting properties between SWCNTs and MWCNTs.

For the doped SWCNTs we consider simulations with coverage (δ) of 5%, 10% and 15% and a partial charge for the doping hydrogen atom of 0.108e, 0.1632e and 0.216e, respectively. The results for all different charges are shown in Fig. 1. For $q_{H_d} = 0.108e$ the value of the contact angle decreases from 96° to 92°, 90° and 86° for increasing percentages of coverage, whereas for $q_{H_d} = 0.162e$ the contact angle decreases to 85°, 79° and 78°, respectively. Finally for $q_{H_d} = 0.216e$ the value is reduced to 73°, 66° and 62°.

It is evident that the contact angle decreases monotonically with the strength of the dipole formed by the surface impurity. In Fig. 2 we show a snapshot from the configuration displaying maximum wetting (case 11: 62°). The degree of wetting is smaller than the one reported in the experiments of Gogotsi and co-workers [12,11,10,16,17]. In these experiments, however, the CNTs may be potentially terminated with hydroxyl and carboxyl groups. This type of impurities may result in a stronger wetting, consistent with findings in [1] and is part of future work. Furthermore the diameters of the tubes fabricated in, e.g. [17] are up to 300 nm and this
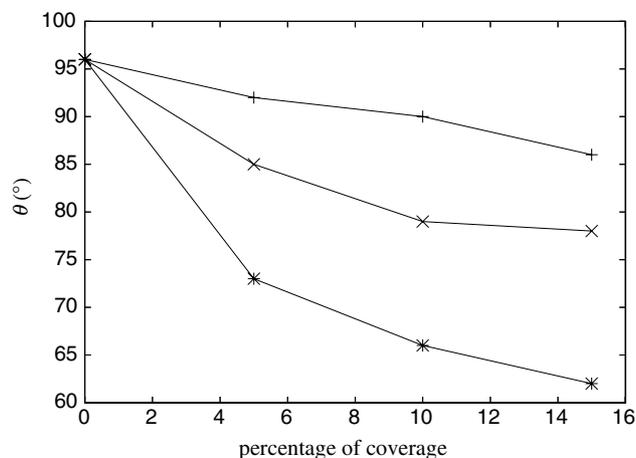

Fig. 1. Contact angle of a water droplet inside a (64,0) SWCNT with chemisorbed hydrogen. The assigned charge values are $q_{H_d} = 0.108e$ (–+–), $q_{H_d} = 0.1632e$ (–×–) and $q_{H_d} = 0.216e$ (–∗–). The contact angle decreases with increasing the partial charge of the doping site and the percentage of coverage.

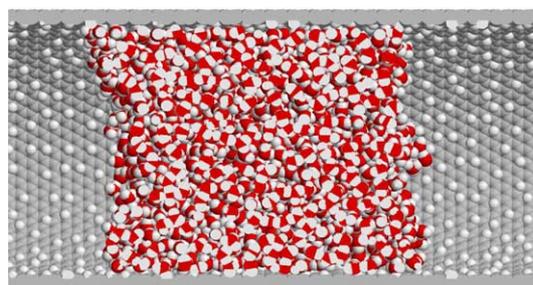Fig. 2. Snapshot from the simulation of case 11 ($q_{H_d} = 0.216e$ and coverage $\delta = 15\%$). Wetting of the surface is observed $\theta = 62°$.

size and doping irregularity does not allow a direct comparison to the simulation setup considered herein. In Fig. 3, we present a closeup of the radial density profiles from the simulations with a coverage (δ) of 15% and different partial charge: $q_{H_d} \in \{0.108e, 0.1632e, 0.216e\}$, corresponding to the cases 5, 8 and 11, respectively. For increasing partial charge we observe an increase in the maximum density and a shift of the location of the maximum towards the surface of the CNT. This observed change is caused by a reorientation of the water molecules located in the vicinity of the fluid-solid interface cf. Fig. 4. We quantify the change in orientation by considering the probability distribution ($p(\cos(\phi))$) of the water dipole moment as function of the cosine to the angle (ϕ) between the dipole moment and the surface normal. The data are sampled at the first peak in the density profile, i.e., in the interval $r = 2.20$–2.45 nm. In the pristine system (case 1) the plane of the water molecules is tangential ($\phi \approx 90°$) to the surface of the carbon nanotube, consistent with previous studies of water external [20] and internal to SWCNTs [13]. For
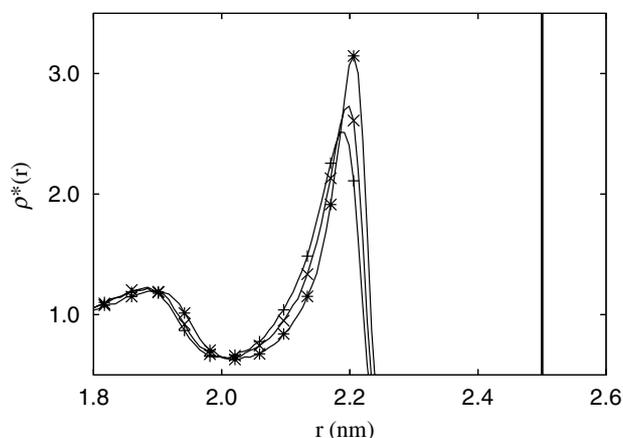
Fig. 3. Radial density profiles for the simulations with coverage $\delta = 15\%$ and partial charge $q_{H_d} \in \{0.108e, 0.1632e, 0.216e\}$ (cases 5 (–+–), 8 (–×–) and 11 (–∗–), respectively). The higher the dipole strength, the closer to the wall nears the first layer of the water molecules. ρ^* is the fluid density normalized with the bulk density of $1\ g\ cm^{-3}$. The vertical line denotes the position of the CNT wall.
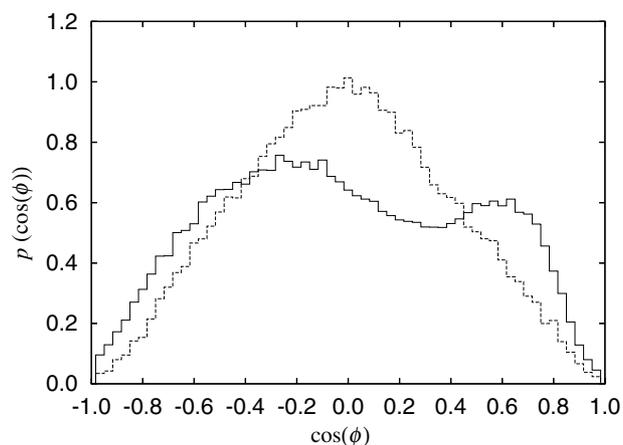

Fig. 4. The probability distribution $p(\cos(\phi))$ of the water dipole moment as function of the cosine to the angle ϕ between the dipole moment and the surface normal is presented for cases 1 (pristine reference case, dashed line) and 11 ($q_{H_d} = 0.216e$ and coverage $\delta = 15\%$). $p(\cos(\phi))$ has been sampled at the first layer of the water molecules (statistical bin of width of 0.25 Å, centered at the first peak of the corresponding radial density profile). In the pristine case 1 the plane of the water molecules is tangential to the CNT wall, whereas in case 11 the hydrogen atoms have a preferential orientation towards the center of the tube.

the doped surface (case 11) the water molecules orient differently and the maximum of the distribution is at an angle $\phi = 107.5°$. In this configuration, with the hydrogens of the water molecules pointing towards the center of the CNT, the resulting force is attractive between the permanent dipoles of the water and the surface leading to increased wetting and a steeping of the density profile towards the CNT wall.

We investigate, furthermore, to what extent the increase in the interfacial wettability is attributed only

to the attractive interactions between the permanent dipoles of the polar water molecules and the surface of the CNTs or in addition to the hydrogen bonding between the water molecules and the doped surface. In order to study these effects we have performed a simulation with a hundred fold shorter bond length of the doping site – effectively modeling a point dipole moment (case 12). The partial charge is adjusted accordingly ($q_{H_d} = 21.6e$) so that the dipole strength is the same as in case 11. In Fig. 5 we present the hydrogen bond profiles for the pristine system (case 1), the doped SWCNTs with increasing partial charge (cases 5, 8, and 11) and effective point dipole study (case 12). We observe that for the water molecules lying at the outermost of the first layer the n_{HB} increases with increasing dipole strength from 2.6 in the pristine case to 3.4, 3.5 and 3.6 in cases 5, 8 and 11, respectively, consistent with the corresponding decrease in the value of the contact angle. In case 12, however, the value of the contact angle increases from 62° in case 11 to 74°. We observe that, due to the small length of the C_d–H_d bond, the number of hydrogen bonds formed from the water molecules lying at the outermost layer is substantially reduced causing this increase in the contact angle value. The hydrogen bond profiles from cases 1 and 12 practically coincide. The results indicate that both the dipole strength and the ability of the water molecules to build hydrogen bonds with the hydrophilic surface have a significant effect on the wetting of CNTs.
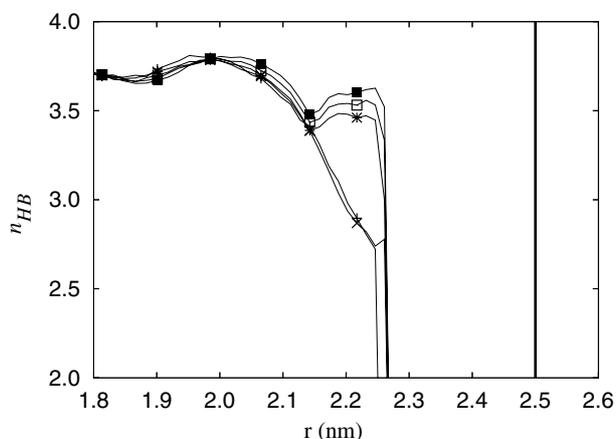

Fig. 5. The hydrogen bond profiles for cases 1 (–+–: pristine reference case), 5 (–∗–: $q_{H_d} = 0.108e$, $\delta = 15\%$), 8 (–□–: $q_{H_d} = 0.1632e$, $\delta = 15\%$), 11 (–■–: $q_{H_d} = 0.216e$, $\delta = 15\%$), 12 (–×–: point surface dipole case). The doping site is also a docking site for the water molecules to form hydrogen bonds with the surface inducing wetting. The higher the dipole strength the bigger the number of hydrogen bonds (n_{HB}) close to the surface. However, the ability of docking is again minimized when we consider point surface dipoles in case 12 and as a result the profiles of cases 1 and 12 practically coincide. The vertical line denotes the position of the CNT wall.

4. Conclusion

In the present study, we showed that surface impurities such as chemisorbed hydrogen sites significantly affect the degree of wetting inside CNT. We identified two key factors responsible for the reduction of the contact angles: the strength of the dipole formed from the doping hydrogen atom and the respective anchoring carbon atom and the hydrogen bonding of the polar water molecules with the impurities at the surface. The contact angle reaches a minimum of 62° at a coverage $\delta = 15\%$ and partial charge of the doping site $q_{H_d} = 0.216e$. The present findings indicate that increased doping results in increased wetting of otherwise hydrophobic CNT surfaces. These results hint at a possible explanation for the increased wetting exhibited by aqueous solutions inside MWCNTs [12,11,10,16,17]. In this direction, ongoing work includes the study of the influence of other impurities on the CNT walls such as OH and COOH groups and their interaction with ionic and other aqueous solutions.

Acknowledgements

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